

Study on New Tool and Indicator of Citric Acid and Sugar Measurement in Some Citrus Fruits

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Abstracts

An experiment was carried out to benchmark suitability of new citrus maturity index (BrimA) against traditional sugar and acid ratio and feasibility of new machine (G-won fruit acidity meter) to measure titratable acidity (TA) against titration method. Six type of citrus fruits (Delight mandarin, Navel orange, Murcott mandarin, Okitsuwase mandarin, Tahitan lime and Eureka lemon) each containing 20 fruits were collected from various source. The total soluble solid was measured using bench-top refractrometer and TA was measured using conventional titration method (0.1N NaOH) and G-won acidity meter. The G-won instrument was found equality effective as conventional method and due to portability and ease of use it could be recommended to researcher, teaching institutions and big farms related to citrus fruit quality analysis. Further, the BrimA index, which takes account of demerit of TSS/TA ratio with addition of fruit taste component while measuring maturity index, was also found promising. The BrimA value of 3.5 for early maturing Satsuma mandarin in mid hills of Nepal could be taken in to a harvesting indicator. Further, there is need of identification of BrimA index value for other Citrus fruit grown in diverse agro-climatic condition of Nepal.

Keywords: *BrimA, mandarin, orange, TSS/TA ratio*

Introduction

Citrus is important fruit crop of the Nepal having production of 218447 mt with productivity of 8.79 mt/ha and grown in all 75 districts in year 2015/16 (MoAD, 2017) with a contribution of 3.9% to Agricultural Gross Domestic Product. Despite this fact, the import of this commodity from other countries was also high with importation of 22202 mt worth of NRs. 914 Crores in year 2014/15. Export of citrus fruit (452 mt) was also recorded in the same year fetching poor price in the market. The reason for such low price was inconsistency in quality of consignment going to the overseas market. At present farmer harvest the citrus fruit based on their judgment when the commodity gets higher price with minimum effort of grading based on size and color. The internal quality attribute such as total soluble solids (TSS) and titratable acidity (TA) are side lined while harvesting and sending such inferior quality fruits to market resulting double negative effect of such consignment i.e. farmers get lower price for his produce, in one hand, while the consumer gets inferior quality produce in other hand. The existence of such issue is partly attributed to the lack of quality standard of fruit for domestic produce and international import in Nepal. There are some quality indicator/standards available in other countries (EU and USA) for citrus fruit (Table 1), which are based on color and TSS/TA ratio (Lado et al. 2014). Use of such indicators in Nepal is limited to quality analysis laboratories, universities and research stations only. Further, the costly equipment and cumbersome protocol for obtaining such indicator (TA) are also causes of limited use in farmers' field. Additionally, the traditionally used quality indicator of citrus fruit, the TSS/TA ratio, is being criticized for lack of repressiveness of the taste (the blend of sweetness and sourness) of citrus fruit (Magwaza and Opara 2015). Further, same TSS/TA ratio could be obtained with different TSS and TA values from same type of fruit having different taste. Therefore, a flavor based indicator named BrimA (pronounced Brimaah), which means brix minus acid, has been proposed by Jorden et al. (2001) and adopted by Citrus industry of California, USA. The formulae for the calculation of this index is $BrimA = \{TSS - k(TA)\}$, where k is a constant factor based on flavor and which is different for crop to crop. For citrus fruit

the constant was proposed as 5 by Jordan et al. (2001) later on Obenland et al (2009) proposed 4 as the best k value while comparing 3,4 and 5 in an extensive study with Navel orange in USA. There is another variant of this BrimA used by Australian and Californian citrus industry where $BrimA = \{TSS - (\%Acid \times 4)\} \times 16.5$ (<https://goo.gl/6bhWjz>). As from the formulae it needs TSS and TA values to calculate the BrimA index and the routine method of obtaining TA is titration using 0.1 N NaOH with phenolphthalein as indicator having pH end point of 8.2. This method is laborious, slow and requires a laboratory to work and therefore, deriving values of TSS/TA as well as BrimA are considered difficult by the farmers. However, in recent years there are development of portable and easy to use acid meters which could remove the barriers of using flavor based indicator by fruit growers in their orchards. The names to refer to such meters are G-won Fruit Acid meter (<https://goo.gl/6K1v1T>, Fig 1a) and Atago Pal Brix-Acid meter (<https://goo.gl/5AFQeV>, Fig. 1b). In this present paper study findings are presented where G-won fruit acid meter was compared with routine TA measurement titration method and suitability of BrimA over TSS/TA indicator was also considered using a range for citrus fruit crops as test samples.

Table 1: Quality standard of some citrus fruit in European Union and USA

Citrus species	TSS (%)	Minimum acidity (%)	TSS/TA ratio	Juice %	Surface color
Mandarin	>8.5	0.3-0.5	6.5-7.5		>1/3
Satsumas			6.5	>33	
Clementines			7	>40	
Nagpur	8.3	0.8			>4/5
Hybrids			7.5		
Sweet oranges	>8.0	0.4-0.7	8-10	>33	>4/5
Navel oranges			8-8.5	>33	
Blood oranges			7	>30	
Others				>35	
Lemons				>20	
Grapefruits	6-7		5.5-7	>35	>2/3

(Modified and adopted from Lado et al. 2014)



Fig 1. a) Citrus Acidity meter from G-won High Tech, Co Ltd, South Korea; and b) Brix acid meter from Atago Company, Japan

Materials and Methods

Five type of citrus fruit: lemon (Eureka), lime (Tahitan), sweet orange (Navel orange), mandarin (Delight, Honey murcott) each 20 in number were purchased from market, while sixth type Satsuma mandarin (Okitsuwase) were collected from orchard of Horticultural Research Station, Dailekh. The fruit were separately squeezed with garlic press to obtain juice, which was filtered with white muslin cloth and collected in a 50-ml glass test tube and later used to analyze TSS and TA reading in duplicate. TSS content of fruits was recorded by temperature compensated bench-top refractometer. The TA reading was taken with two methods; first with G-won Acid meter (Fig 1a). This machine measures electrical conductivity which is influenced by concentration of acid present in the fruit juice. In a dilution container provided with the machine 30 mL distilled water is added with syringe (also provided with

accessory kits). With the help of a pipette from the kit 0.3mL fruit juice is dispensed into the dilution container and mixed well. The mixed solution is poured into the well of machine (Fig 1a) and TA reading was obtained within few seconds. Additionally, the TA reading was also taken using 5-mL juice titrating with 0.1 N standard solutions of sodium hydroxide. The amount of citric acid in juice was calculated using the following formula:

$$\text{TA}\% = \frac{\text{Volume of titrant}^* \times \text{Normality of titrant} \times \text{Milli-equivalent weight of citric acid}^{**} \times 100}{\text{Volume of sample}^*}$$

*Volume of titrant (5 mL); **Milli-equivalent weight of citric acid (0.064)

The BrimA index was calculated using the formulae proposed by Obenland et al (2009).

BrimA1= {TSS-k(TA)}, where k is a constant factor

The another variant of BrimAindex (BrimA2) was calculated using formulae as proposed by California Citrus Association, USA.

BrimA2={TSS-(%Acid x 4)} x 16.5

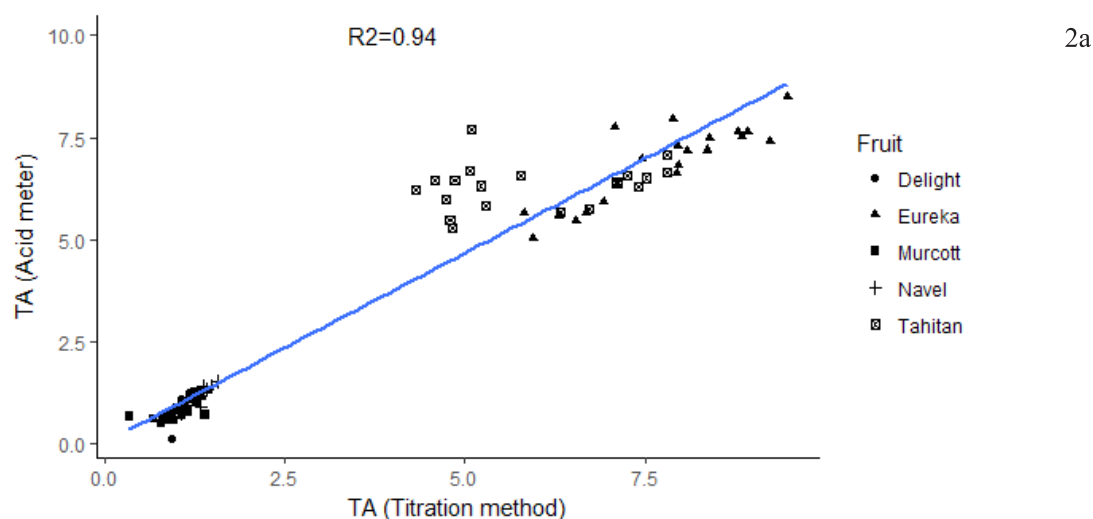
The data were analyzed using Microsoft Excel and graphs were drawn using ggplot2 (v 2.2.1) add on package on R software (v 3.3) platform.

Results and Discussion

Titrateable acid determination method

The G-won acidity meter measures the acidity of citrus fruit close to actual acidity as shown by the association of TA reading between conventional titration method with G-won acidity meter, the ($R^2=0.94$) using TA data of five fruit type (n=100) (Fig 2a). Further while comparing TA measured with two methods with individual fruit group the association was found positive with delight mandarin ($R^2=0.64$), murcott mandarin ($R^2=0.52$), Navel orange ($R^2=0.80$), Eureka lemon ($R^2=0.75$) while it was poor with Tahitan lime ($R^2=0.064$). A similar kind of association was found with Naval orange and mandarin fruit acidity by Obenland et al. (2011). The poor association of reading with high acidity containing fruit could be attributed to low level of variation in the with in Tahitan lime sample with one outlier (Fig. 3) and high amount of acidity present in this group requires dilution of the juice with distilled water which incurs possibility of error during measurement. The evidence of second logic is also supported by the scatter plot where the spread of difference between actual acidity to G-won measured acidity plotted against actual acidity was very high (Fig. 4).

The G-won citrus acid meter is a portable and swift instrument which could be easily taken and used by farmers in the orchards. Further, there are both acid and brix measuring single G-won machine available in the market. However, the price of such machine is an issue costing nearly NRs 200000.00, during this paper written time. At present research and teaching institutions, quality checking authorities as well as big citrus farms could afford this machine for quality check at field to retail shops.



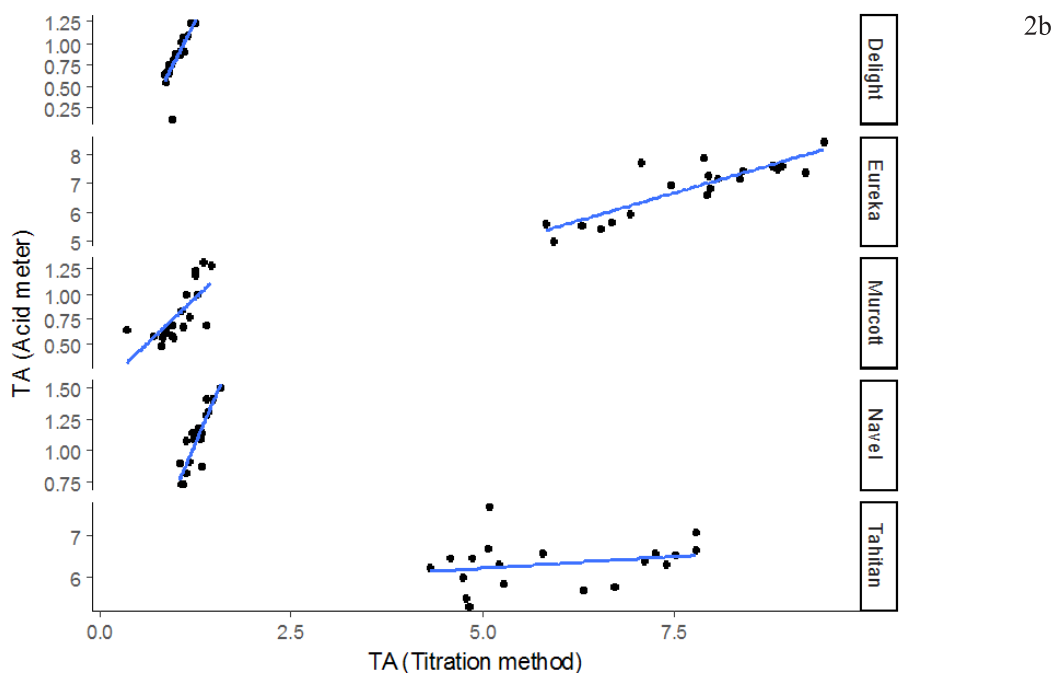


Figure 2 Scatter plot of TA taken from G-won acidity meter with TA from titration method a) five fruit type (n=100) and b) individual fruit type (n=20)

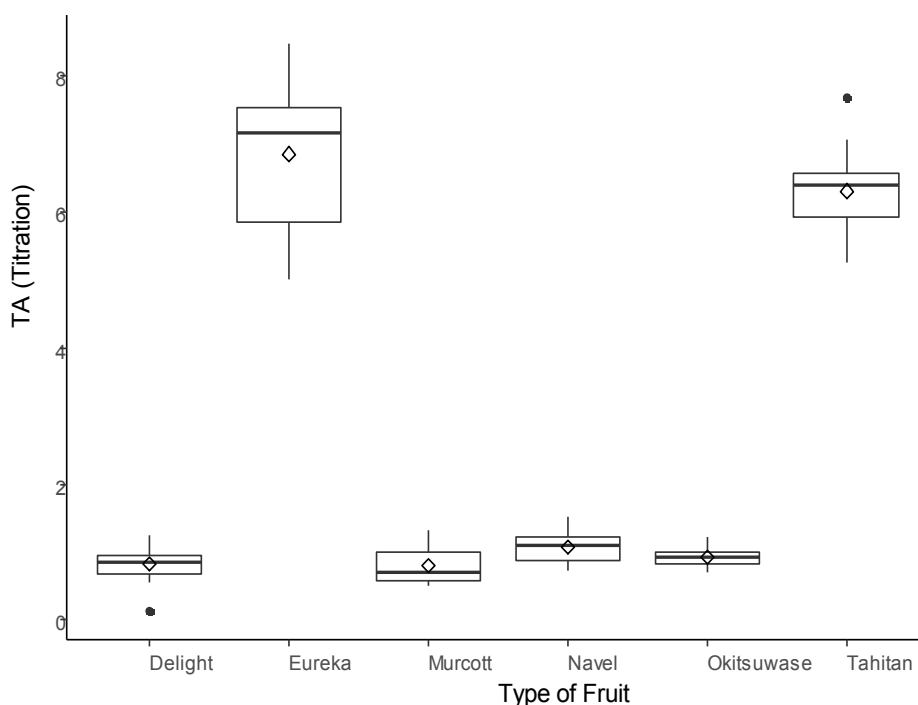


Figure 3 Boxplot of Titratable acidity (TA) of six groups of citrus fruit taken with titration method (n=20, for each group, and diamond shape mark in the box represents mean of the group).

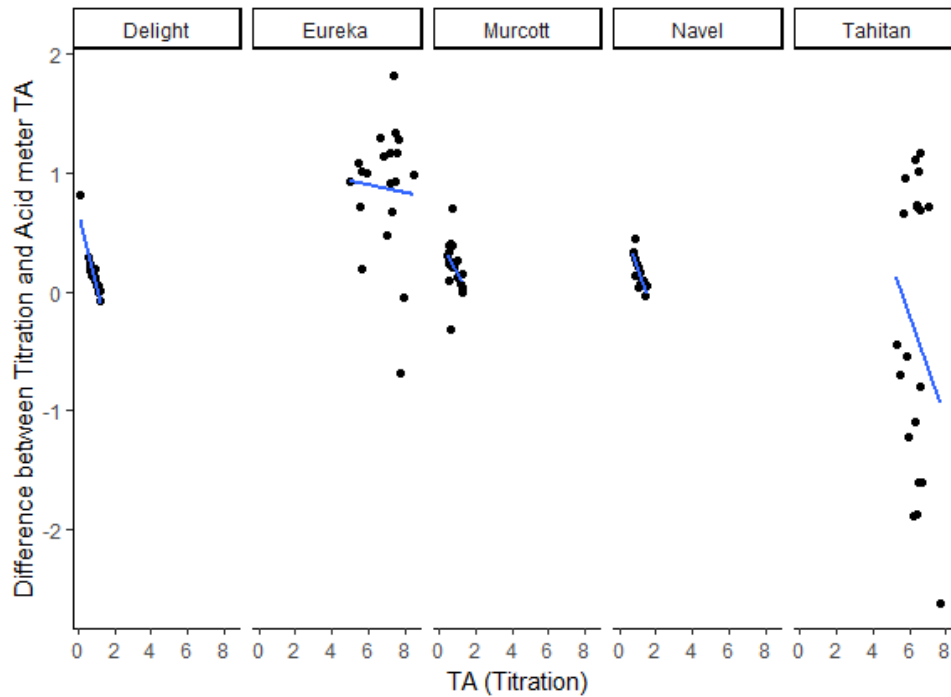


Figure 4 Scatter plot of difference in actual acidity measured by two methods plotted against actual acidity (titration method) where $n=20$ for each group of fruit.

New citrus index

The BrimA1 index value derived using formula proposed by Obenland et al. (2009) was benchmarked against TSS/TA ratio and the association of these indices was found highly positive (Fig. 5a). Similarly, the BrimA1 index was also tested against BrimA2 index and two indices have perfect correlation (Fig. 5b). However, the BrimA index calculated using both formulae showed that negative index values for high acid containing fruits (Fig 6a). The values of such indices were highly negative in BrimA2 compared with BrimA1 index (data not shown). It is obvious to get negative value of BrimA because this value is calculated deducting TA values from TSS and high acid containing fruit contain low amount of TSS resulting negative values. Therefore, BrimA is considered a good ripening indicator mostly for sweet type of citrus fruit (mandarin, sweet orange, grape fruit) rather than sour groups (lime and lemon) (Obeland et al., 2009). This ratio is well adopted for judging harvesting of various cultivars of sweet orange in California, USA and Australia (Magwaza et al., 2015). The BrimA index has also been proposed as good indicator of ripening over TSS, TA and TSS/TA ratio for pomegranate (Fawole and Opara, 2013) and mango (Wongkhot et al., 2012) due to inclusion of fruit taste properties on it. Another study by same author (Chalise and Acharya, 2017) found 7th to 14th September as optimum Okitsuwase mandarin picking time in hills of Dailekh district and the BrimA value of this early variety reaches 3.5 during that time (Fig 6b).

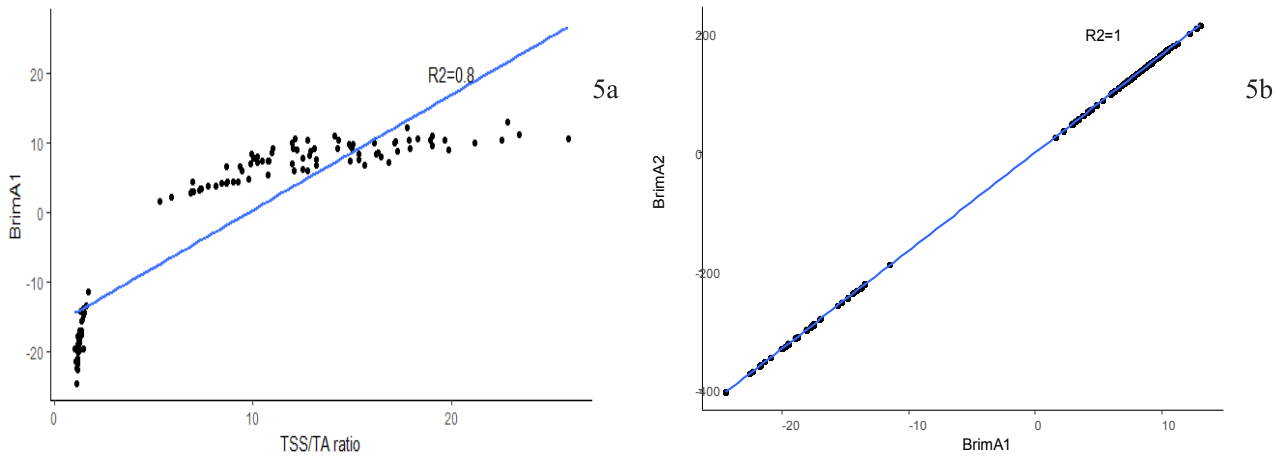


Figure 5 Scatter plot of BrimA1 value of various type of citrus fruit against a) TSS/TA ratio and b) Brim A2 index

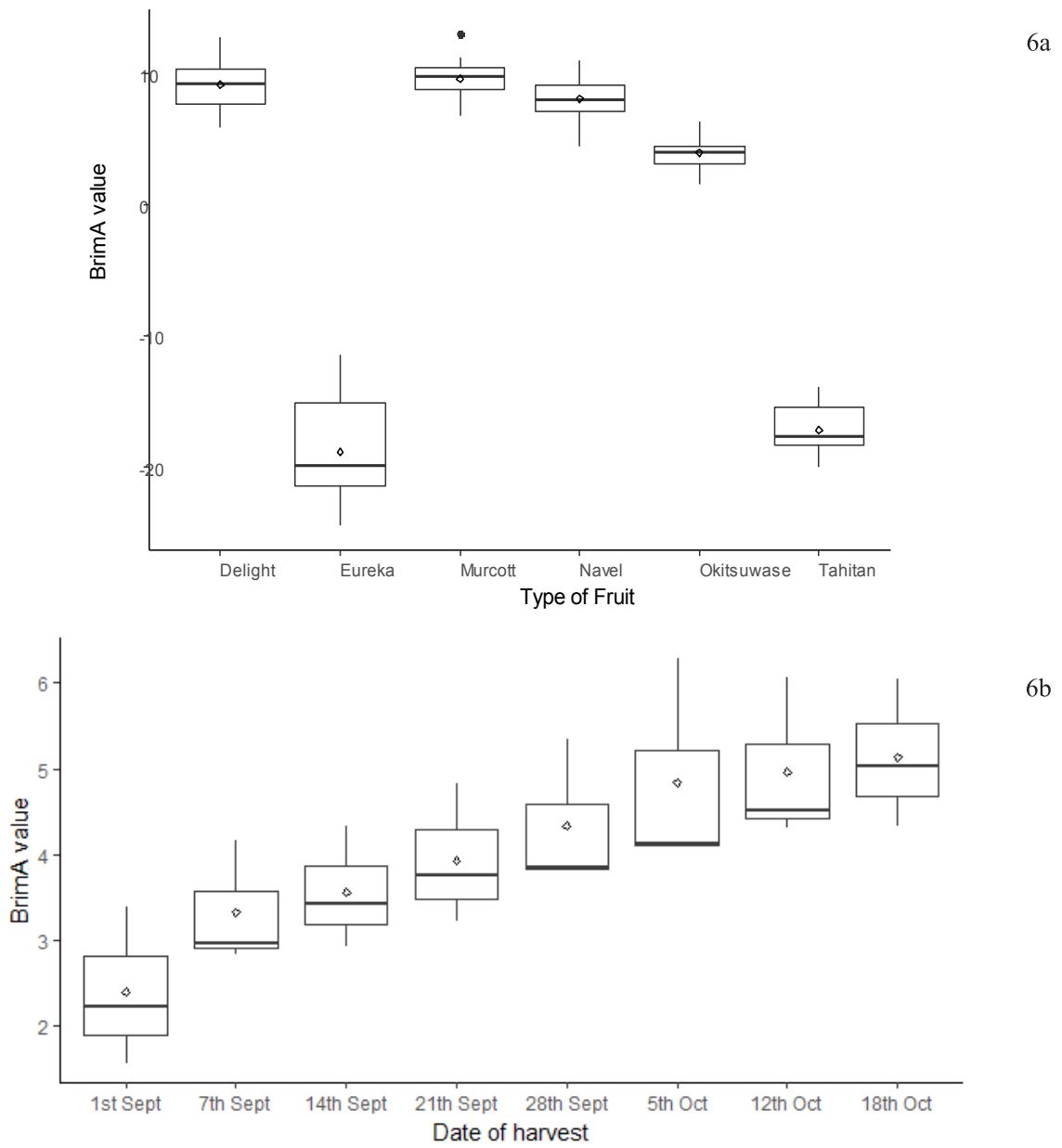


Figure 6 Boxplot of Brim A1 index for a) six types of citrus fruit and b) Okitsuwase mandarin on different date of harvesting, diamond shape in the middle of the box represents mean value.

Conclusion

The G-won acidity meter is very efficient in measuring TA for citrus fruit having diverse ranges of acidity. However, extra care should be taken while measuring TA of high acidity fruit as the fruit juice needs dilution with distilled water due to measuring limit of this instrument. The brimA index (BrimA1) is as good as TSS/TA ratio and due to inclusion of fruit taste aspect makes this index promising over TSS/TA ratio. Therefore, it could be recommended as a maturity index for citrus fruit having low level of acidity. Further, there is need of identification of BrimA index value for each of citrus fruit grown in diverse agro-climatic condition of Nepal.

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